云 南 植 物 研 究 1998, 20 (3): 369~373
Acta Botanica Yunnanica

印度蛇菰的三萜成分*

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摘要 从我国民间药用植物印度蛇菰 (*Balanophora indica* (Arn.) Griff.) 中分离得到7个化合物,经鉴定为: 棕榈酰 β-香树酯 (蛇菰素A)、棕榈酰羽扇豆烯醇酯 (蛇菰素B)、乙酰β-香树酯、乙酰羽扇豆烯醇酯、β-香树脂酮、羽扇豆烯酮及棕榈酸。运用光谱和化学的方法对它们的结构进行解析。其中羽扇豆型萜为首次自该植物中分得; 蛇菰素A和B具有较强的护肝作用。
关键词 印度蛇菰, 三萜酯, 蛇菰素A, 蛇菰素B
分类号 Q 946

Triterpene Constituents from *Balanophora indica*

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Abstract From herbs of the Chinese folk medical plant *Balanophora indica*, seven compounds: β-amyrin palmitate (balanophorin A), lupeol palmitate (balanophorin B), β-amyrin acetate, lupeol acetate, β-amyrone, lupeone and palmitic acid were isolated. Their structures were elucidated by the basis of spectral and chemical evidences, respectively. The compounds of lupane were obtained from *B. indica*, firstly. Balanophorin A and B exhibited strong activity against liver damage induced by CCl_4.
Key words *Balanophora indica*, Triterpene ester, Balanophorin A and B

Balanophora indica (Arn.) Griff. was a kind of parasitic plant with root, belong to species of the family Balanophoraceae. It is used as a folk medicine plant for the tonics and hemostatic, indigenous to the province Yunnan. To our knowledge, the biologically active principle and constituents from this plant, have not been described as yet. Therefore we studied on the constituents of it. Here we report on the investigation of the isolation and structural elucidation of two triterpene esters from this plant.

RESULTS AND DISCUSSION

The petroleum benzine extract of the herbs of *Balanophora indica* (Arn.) Griff, was subjected to repeated column chromatography on silica gel and aluminum oxide, to give 7 compounds: β-amyrin 3-palmitate (1, balanophorin A), β-amyrone (2), β-amyrin 3-acetate (3), lupeol 3-palmitate (4, balanophorin B), lupeone (5), lupeol 3-

* 中国科学院昆明植物研究所植物化学开放实验室基金资助
1997-09-17 收稿, 1998-04-21 接受发表

acetate (6) and palmitic acid (7). The yield of balanophorin A and B were 1.21% and 1.34%, respectively.

Balanophorin A showed a molecular ion peak at m/z 665cm^{-1}(M + 1, $C_{46}H_{80}O_2$) in the mass spectrum. The IR spectrum showed at 1710, 1165, and havent at 3300 ~ 3500cm^{-1}, indicating the presence of a carbonyloxy group (O = C – O). The ^{1}H – NMR spectrum appeared one olefinic proton signal at δ5.15(1H, brs), one oxygen – bearing carbon proton signal at δ4.47(1H, br, t J = 7.4Hz) in the lowfield range; and nine methyl proton at δ 1.11(3H, s), 0.94(3H, s), 0.93(3H, s), 0.84(15H, brs, 5 × CH_3), 0.80(3H, s); seventeen methylene protons at δ 1.23(34H, brs, 17 × CH_2), and the great majority protons signal showed gather at δ 0.80 – 2.28 rang in the highfield. It suggested that balanophorin A could be an tritepene ester derivative. The IR spectrum absorption at 1370, 1350, were indicated that balanophorin A could be belong to the β – amyrin type triterpene ester derivative (Snatzke *et al*, 1962). The ^{13}C NMR and DEPT spectrum of balanophorin A revealed one carbonyl carbon(δ 173.4), nine methyl carbons (δ 24.3, 16.8, 25.9, 28.0, 32.4, 23.7, 14.1), six quaternary carbons (δ 38.2, 39.8, 37.1, 41.7, 32.6, 34.8), four methine carbon [δ 80.5(bearing an oxygen atom), 55.2, 47.5, 47.2] and two loefinic carbons (δ 121.6d, 145.1s). These data can be accommodated on the β – amyrin type triterpene having long chain fatty acid. The EI – mass spectrum of balanophorin A showed a characteristic fragment ion for the loss of palmitic acid at m/z 218(base peak). On comparison of the ^{13}C NMR and ^{1}H – NMR spectrum of balanophorin A with that of β – amyrin (Bhattacharyya *et al*, 1986), was identified as β – amyrin 3 – palmitate (1). The EI – mass spectrum of the alkaline hydrolysis product was corresponding with that of β – amyrin, and further confirmed that balanophorin A should be assigned to the β – amyrin ester. From the above evidence, the structure of balanophouin A was established to be β – amyrin 3 – palmitate.

Balanophorin B was calculated for $C_{46}H_{80}O_2$ by the FABMS and ^{13}C NMR spectrometry. The IR spectrum appeared two absorption at 1710(C = O), and 1625(C = C). The ^{1}H NMR spectrum was quite similar to that of balanophorin A, but it showed two olefinic proton signals at 4.66(1H, s), 4.54(1H, s); eight methyl proton at δ 0.76(3, s), 0.81(9H, s, 3 × CH_3), 0.84(3H, s), 0.92(3H, s), 1.00(3H, s), 1.66(3H, s); and seventeen methylene protons at δ 1.23(34H, brs, 17 × CH_2). The ^{13}C NMR and DEPT spectrum revealed one carbon (δ 173.5), two olefinic carbons (δ 109.4t, 150.8s), five quaternary carbons (δ 38.9, 4.09, 38.1, 42.7, 43.0), and six methine carbon (δ 80.7, 55.5, 50.4, 37.2, 48.4, 48.0). It expressed that balabophorin B could be a lupeol type derivative. The EI – mass spectrum of it exhibited a characteristic fragment ion for the loss of plamitic acid at m/z 409(M – 256), 239, 257, amd 426. It was identified as lupeol 3 – palmitate (4) by comparison of the data of NMR with lupeol (Dreyer *et al*, 1972). Alkaline hydrolysis of it yields a triterpene compound. The EIMS of the triterpene was corresponding with that of lupeol. The structure of it was established to be lupeol 3 – palmitate, again. This compound was obtained from *B. indica*, firstly (Yadagiri *et al*, 1984; Chengalur *et al*, 1976).

Balanophorin A and B exhibited strong activities against liver damage induced by CCl_4 in mice (Lin *et al*, 1988).

EXPERIMENTAL

General procedures The NMR spectra were performed choroformed using TMS as int. standard at 400MHz with a Brucker AM – 400 instrument. The carbon type was determined by DEPT experiments. IR spectra were recorded in KBr pellets on a Perkin – Elmer 577 interferometer. EIMS and FABMS: positive, direct inlet 70eV on VG Autospec instrument. For CC, silica gel(200 ~ 300 mesh, Qingdao) and aluminum oxide (neutral, 200 ~ 300 mesh, Shanghai). TLC precoated silic gel plate HF_{254}(0.25mm in thickness).

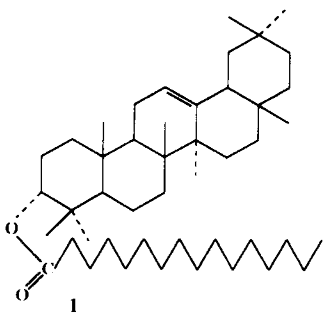
Plant material The whole plant of *Balanophora indica* (Arn.) Griff were collected in Xishuangbanna, Yunnan province, in October, 1996, and identified by Mr. Cui Jing – yun, Xishuangbanna Tropical Botanic Garden, the Chinese Academy of Scinences, where the herbarium specimen has been deposited.

Identification of the known triterpenes　All of the known were identified by comparison with authentic samples by their NMR or MS spectra data.

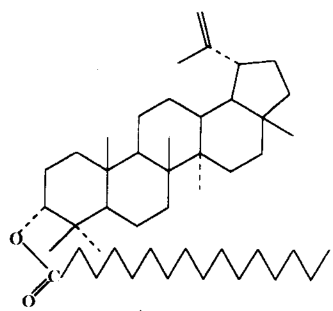
Extraction and Separation of triterpenes　The dry whole plant powered material (700 g) was extracted with petroleum benzine yielding, after evapn, a brown yellow oil residue (80 g). The petroleum benzine extract was dissolved in benzene and extracted with methanol. The benzene layer, on evapn of the solvent, 46 g residue was obtained. The benzene extract chromatographied on a column of silica gel with petroleum benzine - acetone (20:1 ~ 2:1) to give 3 fractions in increasing of polarity. Fraction 2(29 g) was purified by CC on aluminum oxide (neutral) with benzene - methanol (4:1) to furnish balanophorin A(8.5 g) and B(9.4 g). Fraction 3 was separated similarly as that for fraction 2 to afford β - amyrin 3 - acetate (40 mg), β - amyrone(21 mg). And lupeol 3 - acetate(34 mg), lupeone(25 mg). Palmitic acid was obtained from fractoin 1.

Balanophorin A (1). Amorphous white powders (Me_2CO), mp 77℃, dissolved in chloroform, petroleum benzine and benaene. IR $\nu_{max}^{KBr}cm^{-1}$: 2900, 2825, 1710, 1450, 1370, 1350, 1235, 1165, 1085, 980, 710. FABMS(m/z): 665(M + 1). EIMS(m/z): 665, 409, 218(base peak), 257, 239, 203, 190, 175, 109, 69. ^1H NMR($CDCl_3$): δ 5.15(1H, brs, 12 - H), 4.47(1H, t, J = 7.4Hz, 3 - H), 2.26(2H, t, J = 7.4Hz, 2' - H), 1.23(34H, brm, CH_2), 1.11(3H, s, 27 - CH_3), 0.94 (3H, s, 30 - CH_3), 0.93(3H, s, 29 - CH_3), 0.84(15H, brs, CH_3), 0.80(3H, s, 16' - CH_3). ^{13}C NMR data see table. Balanophorin A(20 mg), was treated with NaOH - H_2O(2.0 g NaOH dissolved in 20 ml H_2O) at 160℃ for 12 hr. The reaction mix was extracted with $CHCl_3$, after evapn, obtained a residue. The EIMS spectra of the residue exhibited a fragment ion peak at m/z 426, 218(base peak).

Balanophorin B (4). Amorphous white powders (Me_2CO), mp 68 ~ 69℃. IR$\nu_{max}^{KBr}cm^{-1}$: 3040, 2900, 2825, 1710, 1625, 1450, 1440, 1438, 1370, 1165, 970, 900, 710. EIMS (m/z): 665(M + 1), 409, 426, 257, 239, 218, 95, 68, 55(base peak). ^1H NMR($CDCl_3$): δ 4.46(1H, s, 29 - H), 4.54(1H, s, 29 - H), 4.44(1H, dd, J = 10.5, 5.6Hz, 3 - H), 1.23(34H, brm, CH_2), 1.66(3H, s, 30 - CH_3), 1.00(3H, s, 27 - CH_3), 0.92(3H, 24 - CH_3), 0.84(3H, s, 29 - CH_3), 0.81(9H, s), 0.76 (3H, s), 0.76(3H, s, 16' - CH_3), 2.26(2H, t, J = 7.6Hz, 2'- CH_2), 2.31(1H, m, 18 - H). ^{13}C NMR data see table. Balanophorin B(20 mg), was treated with NaOH - H_2O(2.0g NaOH dissolved in 20ml H_2O) at 160℃ for 12 hr. The EIMS spectra of the product exhibited a fragment ion peak at m/z 426, 189, 203.



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β - Amyrone (2). $C_{30}H_{48}O$, M424. Colorless needles (MeOH). The EIMS, ^1H and ^{13}C - NMR spectra data were identical to the published reference spectra data of β - amyrone (Gonzalez *et al*, 1981).

β - Amyrin acetate (3). $C_{32}H_{52}O_2$, M468. Colorless pillars (Me_2CO), mp 236 ~ 237℃ Similary, the EIMS ^1H and ^{13}C - NMR spectra data were identical to those of the reference compound β - amyrin acetate(Seo *et al*, 1975).

Lupenone (5). $C_{30}H_{48}O$, M424. White needles (MeOH). The EI - MS, ^1H and ^{13}C - NMR spectra were corresponding with that of lupene 3 - one (Budzikiewicz *et al*, 1963).

表1 蛇菰素A和B的 ^{13}C NMR数据

Table 1 ^{13}C NMR data of balanophorin A and B

C (碳序)	Balanophorin A 蛇菰素A	Balanophorin B 蛇菰素B	C (碳序)	Balanophorin A 蛇菰素A	Balanophorin B 蛇菰素B
1	37.7 t	37.8 t	21	31.9 t	29.4 t
2	23.6 t	23.4 t	22	36.8 t	40.0 t
3	80.5 t	80.7 t	23	28.4 q	27.5 q
4	38.2 s	38.54 s	24	16.8 q	16.3 q
5	55.2 d	55.5 d	25	15.5 q	16.3 q
6	18.2 t	18.3 t	26	16.8 q	16.3 q
7	33.3 t	34.3 t	27	25.8 q	14.5 q
8	39.8 s	40.9 s	28	28.0 q	18.3 q
9	47.5 d	50.4 d	29	32.4 q	109.4 t
10	37.1 s	38.1 s	30	23.7 q	19.4 q
11	23.5 t	21.0 t	1′	173.4 s	173.5 s
12	121.6 d	25.2 t	2′	34.9 t	34.8 t
13	145.1 s	37.2 d	3′	25.1 t	25.2 t
14	41.7 s	42.7 s	4′	29.3 t	29.3 t
15	26.9 t	27.5 t	⋮	⋮	⋮
16	26.2 t	35.6 t	⋮	⋮	⋮
17	32.6 s	43.0 s	13′	29.7 t	30.8 t
18	47.2 d	48.4 d	14′	31.0 t	31.9 t
19	46.8 t	48.0 d	15′	22.7 t	22.7 t
20	34.8 s	150.8 s	16′	14.1 q	14.5 q

Measured in $CDCl_3$, ppm.

Lupeol acetate (6), $C_{32}H_{52}O_2$, M468. Colorless pillars (MeOH), mp 217 ~ 218℃. The EIMS and NMR spectra data were identical to those of the reference compound lupeol 3 - acetate (Wenkert *et al*, 1978).

Palmitic acid (7). $C_{16}H_{32}O_2$, M256. Colorless powders (MeOH). The EIMS and NMR spectra were corresponding with that of palmitic acid (Vanderlan *et al*, 1991).

Acknowledgements We are grateful to the Instrument Analysis Group of the Phytochemistry Department, Kunming Institute of Botany for measurements of all spectra.

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10	动物学报	264	10	实验生物学报	0.2397

1. 数据来源：中国科学院文献情报中心中国科学引文数据库 1996 年数据。本表由中国科学引文数据库统计编制。
2. 被引频次是对被中国科学引文数据库 1996 年 582 种来源期刊所引用的数千种中国出版的中英文期刊进行频次统计后编制而成的。
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4. 本着尊重原始数据的原则，本表对变名期刊未作任何合并处理。